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Reactive Ion Etching of Aluminum/Silicon in BBr_3/Cl_2 and BCl_3/Cl_2 Mixtures

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ABSTRACT

Boron tribromide mixed with chlorine, BBr_3/Cl_2, a novel gas mixture for dry etching of Al and Al alloys, has been studied in a hexagonal cathode reactive ion etching system. Etch rates, selectivities, profiles, and linewidth loss were determined as a function of feed gas composition, dc self-bias, and reactor load in a Box-Behnken experimental design. Response surface analysis indicates a window exists in the experimental parameter space where significant improvements in selectivity can be achieved without sacrificing anisotropic profiles. For example, anisotropic etching can be achieved with BBr_3/Cl_2 mixtures while maintaining Al/SiO_2 and Al/photoresist etch rate ratios of 33:1 and 15:1, respectively. The achievable selectivities in a conventional mixture of BCl_3/Cl_2 were 13:1 and 2.5:1 for comparable anisotropic etching. Optical emission and mass spectrometry measurements were used to aid in an investigation of the kinetics of BBr_3/Cl_2 etching of Al and Al_2O_3 films. Scanning Auger microprobe analysis was performed on the postetched substrates. A kinetic model is proposed to account for variations between BBr_3/Cl_2 and BCl_3/Cl_2 RIE etching of Al and Al alloys.

Etching of Al and Al alloy thin films in plasmas containing halides is now well-known (1), yet the difficulties inherent in this task continue to represent a formidable problem in the fabrication of fine line integrated circuits. A production worthy Al/Si etch process must be able to remove the native oxide that initially resides on the Al surface, etch Al/Si at a high rate, and etch the masking and underlying materials at an acceptably low rate, *i.e.*, the selectivities must be high. Most processes for high resolution, reproducible plasma, or reactive ion etching (RIE) of Al and Al alloys rely on chlorine (Cl_2) in combination with a Cl-bearing gas such as boron trichloride (BCl_3), carbon tetrachloride (CCl_4), silicon tetrachloride ($SiCl_4$), or chloroform ($CHCl_3$) (1-3). Of these, BCl_3/Cl_2 mixtures have become popular due to their ability to etch aluminum while providing freedom from polymeric deposits (3). Despite the fact that BCl_3/Cl_2 plasmas have the rather severe drawback of poor selectivity, they, along with the other above chlorinated etchants, remain the standard industrial process gases. This is in a large way due to the dearth of information regarding the behavior of other halogenated gases in the plasma environment. In this paper we report findings on the use of an alternative boron halide, BBr_3, in combination with Cl_2, which shows great promise for overcoming some of the difficulties inherent in conventional RIE of Al/Si films.

Recently, three reports (4-6) have examined the feasibility of employing BBr_3 or Br_2 in place of the more established BCl_3 or Cl_2 gases used for RIE of Al and Al alloy films. The physical/chemical properties of etchant gases containing Br indicate it is a reasonable alternative for Al plasma etching. The most recent of these reports includes speculation on mechanisms which could account for the observed etching trends (6). Although valuable trends in the etch characteristics of gases containing Br are now known, practical details on the relationship of process variables to profile control, photoresist erosion, and selectivity over Si and SiO_2 are still unclear. This study reports on a series of Al/Si etch process experiments involving variations in feed gas composition, dc self-bias voltage, and reactor loading during reactive ion etching of aluminum alloys (Al/1% Si) in BBr_3/Cl_2 mixtures. Most etch processes for Al films etch Si at a high rate so that the small amount of Si in the alloy to prevent spiking causes no major etching differences or problems (for this reason, and simplicity, Al/Si and Al will be used interchangeably in further references). A Box-Behnken (7) experimental design was used to specify the experimental matrix, and response surface analysis was used to determine etch rate, linewidth loss, and selectivity responses to changes in the independent process variables. Concurrent with these experiments, BCl_3/Cl_2 gas mixtures were studied in order to compare the results for BBr_3/Cl_2 etching to an established process. These RIE studies were all performed in a hexagonal cathode reactor.

Comparisons between the results of BBr_3/Cl_2 and BCl_3/Cl_2 RIE of Al films are then used, along with additional diagnostic information gained by mass and optical emission spectrometry, to investigate the reaction mechanisms important to the aluminum etch process. Those kinetic steps or features which account for the particular contrast in the ability of the two etchant gases to selectively etch Al are examined in detail.

Experimental

One hundred millimeter diameter Si wafers were coated with 1 μm of Al/1% Si by sputter deposition for use in Al_2O_3 and Al etch rate determination. These wafers were coated with 1.5 μm of KTI 1450 positive photoresist and patterned with 2, 3, 4, and 5 μm lines and spaces. Following development, samples were baked at 140°C for 60 min. A second type of test wafer for Si and SiO_2 etch rate determination was also prepared, in a manner described by Light (3). Additionally, separate photoresist and Al loading experiments were conducted by placing four to sixteen photoresist or Al-coated wafers in place of SiO_2-coated dummy wafers in the reactor.

The BBr_3 used in these experiments came from a liquid source provided by J. C. Schumacher Company. The source was kept at a temperature of 35°C by a constant temperature unit and the feed lines were wrapped with heat tape to prevent condensation. A 0.020 in. mass flow controller orifice was chosen to allow sufficient flow at the vapor pressure of the BBr_3 (about 100 torr at 35°C). Smaller standard orifices had proven inadequate. The etching reactor was a Plasma Therm Hexetch 640 RIE system with a 3000W, 13.56 MHz RF power supply. A dc self-bias voltage comparison to the BCl_3/Cl_2 production process now in place, the total flow and total pressure were set at 50 sccm and 10 mtorr, respectively. The electrode temperature was set at 25°C and the chamber temperature was set at 45°C.

Due to limitations on the number of patterned samples available for this study, the maximum patterned wafer load was set at 12 wafers. Previous experience has shown that response trends valid at a 12-wafer load are also valid at loads up to a full 24 wafers. A description of more extensive loading experiments may be found with additional details on the use of BBr_3 in the RIE process in the work by Bell (8) and Bell *et al.* (9). Additional description of the RIE process and the BCl_3/Cl_2 etching technique in this reactor have been reported by Light (3). No precautions were taken to prevent post-RIE corrosion and no serious corrosion was observed. The current method for dealing with post-RIE corrosion concerns in the BCl_3/Cl_2 process is an *in situ* O_2 strip.

The three factor Box-Behnken experimental design employed in these studies involved varying dc self-bias voltage from −100 to −200V, percent chlorine from 12 to 48%, and reactor load from 2 to 12 wafers in the manner depicted in Fig. 1. The design was symmetric with each factor given equal weight. The design also included replicate points for experimental error estimates and sufficient degrees of freedom to permit evaluation of the lack-of-fit error for the model. The Box-Behnken experimental design, as implemented here, allowed exploration of quadratic response surfaces, while minimizing the number of experiments involving each etchant mixture. The additional photoresist and Al loading experiments mentioned above were performed at the center point of the Box-Behnken experimental design.

Mass spectrometry and optical emission spectrometry (OES) were used to monitor species relative concentration and optical emission during the course of these experiments. A special flange and orifice were designed to couple a differentially pumped UTI Model 100C quadrupole mass spectrometer to a standard window port on the Hexetch 640 bell jar. The mass spectrometer was approximately 30 cm removed from the bell jar window port. The mass spectrum range recorded during the study was limited to low molecular weight species (less than 200 amu) based on previous reports (2) indicating they would be the likely observable dissociation products downstream of the discharge and based on the known cracking patterns of the parent molecules (10). Emission spectra from 200 to 800 nm were taken with a PT-Analytical Model PSS-100 spectrophotometer. Etched substrates were examined by scanning Auger microprobe (SAM) in an attempt to compare level, type, and location of contamination or residue left on surfaces after etching.

Results and Discussion

RIE response behavior of BBr_3/Cl_2 and BCl_3/Cl_2.—Data from the Box-Behnken experiments were analyzed employing conventional response surface methodology and an experimental design software package (11). The most successful fit was found with a quadratic model, although a note of caution is in order here. The small number of experiments in the Box-Behnken design has yielded a quadratic model that represents the data well in the area of interest, but which has moderately high residuals in some areas. The quadratic model assumed the form

$$Y_n = b_{0_n} + \sum_{i=1}^{k} (b_{i_n} x_i) + \sum_{i=1}^{k} \sum_{j=1}^{i} (b_{ij_n} x_i x_j) \qquad [1]$$

where: Y_n = the nth response variable (n = 1-6), x = ith variable factor, b_{i_n} = ith model coefficient for the nth response variable, and k =number of independent variables. Table I, shown above, contains the R^2 values for variance about the mean derived from an analysis of the Box-Behnken matrix of data on BCl_3/Cl_2 and BBr_3/Cl_2. Linewidth loss and selectivity responses in BBr_3/Cl_2 do not correlate as well as the other responses with a simple quadratic model. However, the poor fit for selectivity may be due in large part to resolution limitations of the Alpha Step 100 profilometer used as the etch depth measurement tool, and the relatively large experimental measurement errors which can result if the photoresist and SiO_2 etch rates are small. The model lack of fit for linewidth loss cannot be readily explained except to say that the mechanism by which linewidth loss occurs in BBr_3/Cl_2 is more complex compared to BCl_3/Cl_2 and that a higher order interaction model may be needed to accurately represent that data. Curves and response surface plots were obtained from the model and are represented in Fig. 2-12.

Table I. R^2 values for the quadratic model

	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
BBr_3/Cl_2	0.99	0.93	0.81	0.90	0.82	0.55
BCl_3/Cl_2	0.96	0.97	0.94	0.97	0.97	0.92

Y_1, native oxide etch rate.
Y_2, Al etch rate.
$Y_{3\text{-}5}$, selectivities to photoresist, Si, and SiO_2, respectively.
Y_6, linewidth loss.

Al_2O_3 etching.—Figures 2 and 3 illustrate that the native oxide etch rate in BBr_3/Cl_2 is approximately 1/2 that of BCl_3/Cl_2 mixtures under comparable conditions. It can be seen that native oxide etching in both mixtures increases with increases in dc self-bias and decreases with increases in Cl_2 fraction in the feed gas. A significant interaction between reactor load and percent Cl_2 was observed in native oxide etching with BBr_3/Cl_2, but was absent with BCl_3/Cl_2. At low Cl_2 fraction in BBr_3/Cl_2 mixtures, no loading effect on the native oxide etch rate was observed. However, as the Cl_2 fraction was increased, increases in reactor load slowed the native oxide etch rates, indicating a depletion of the active agent for native oxide etching.

Work by Keaton and Hess (6) indicates that the ability of pure BBr_3 plasmas to remove native aluminum oxide layers is significantly less than that of pure BCl_3 plasmas. Thus, it is not surprising to find that native oxide etch rates during RIE of Al in BBr_3/Cl_2 are reduced as well, compared

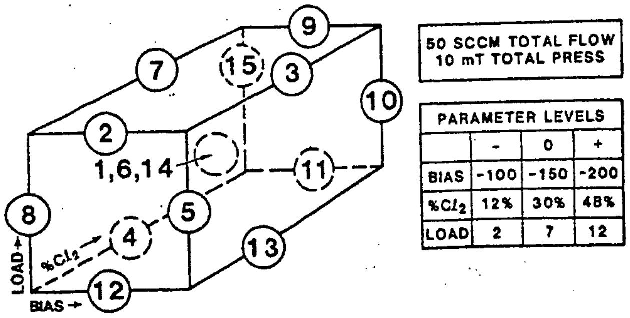

Fig. 1. Box-Behnken randomized experimental run sequence

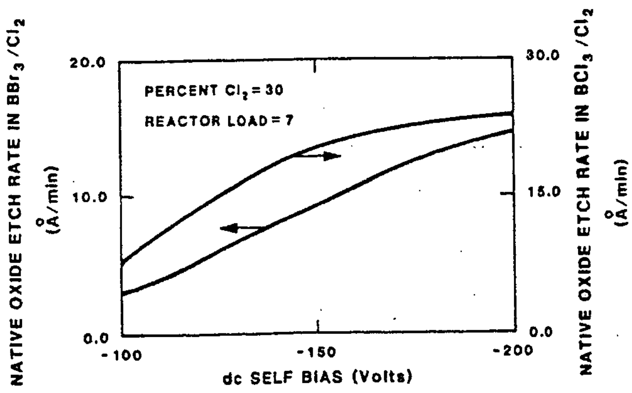

Fig. 2. Native Al oxide etch rate as a function of dc self-bias voltage in BX_3/Cl_2.

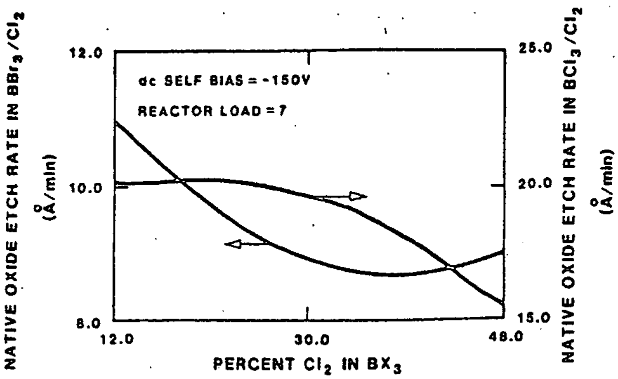

Fig. 3. Native Al oxide etch rate as a function of percent Cl_2 in BX_3/Cl_2.

to BCl_3/Cl_2. Keaton and Hess suggest the differences between the two gases can be explained in terms of different rate controlling steps during the reaction sequence with native oxide. Removal of native oxide with BCl_3 can be explained either through an ion bombardment mechanism or chemical reaction of BCl_x species, whereas, native oxide etching with BBr_3 appears to be much more chemical in nature involving reduction of the surface aluminum oxide through a surface temperature dependent, chemical reaction with BBr_x species. The similar dependence of BBr_3/Cl_2 and BCl_3/Cl_2 RIE on dc self-bias in this study indicates that aluminum oxide removal in either plasma requires ion assistance as well as a chemical reducing agent. The results of the reactor loading experiments suggest BBr_3/Cl_2 mixtures have difficulty etching native oxide due to the lack of suitable species capable of reducing the oxide during RIE, in addition to any unfulfilled surface activation energy requirement.

Al etching.—A comparison of BBr_3/Cl_2 and BCl_3/Cl_2 reactive ion etching of the Al film is shown in Fig. 4-6. The etch rate of Al increases with percent Cl_2 in both mixtures and with dc self-bias voltage, but decreases as a function of reactor loading. The similar Al etching behavior of both gas mixtures suggests etching proceeds via the same mechanism and that Cl_2 is a major source of etching species. However, the etch rate for BBr_3 mixtures is higher than that of BCl_3 mixtures under most conditions, indicating Br liberated by the dissociation or reaction of BBr_3 may be an important etchant species as well. Although it can be inferred from the response to increases in dc self-bias that ion bombardment plays a role in enhancing Al etching in both gas mixtures, the differences in the ability of the two gas mixtures to etch Al appears to be more rate limited by the concentration of active etchant species, which are depleted with reactor loading. The role of ion bombardment in Al etching is likely one of energetically cleaning the surface of etch inhibitors. A significant interaction between dc self-bias and reactor load exists for BBr_3/Cl_2, indicating that the rate-limiting step in Al etching is influenced by the energetics of ion bombardment. At low bias levels, removal of surface residues through ion bombardment appears to be inefficient and rate limiting. At high bias levels, energetic ion bombardment is effective in cleaning the surface and reactant depletion becomes rate limiting. Although electrode temperature variations were not studied, it may be speculated that adding energy to the process through higher electrode temperature may have a similar effect to that caused by adding energy through higher dc self-bias.

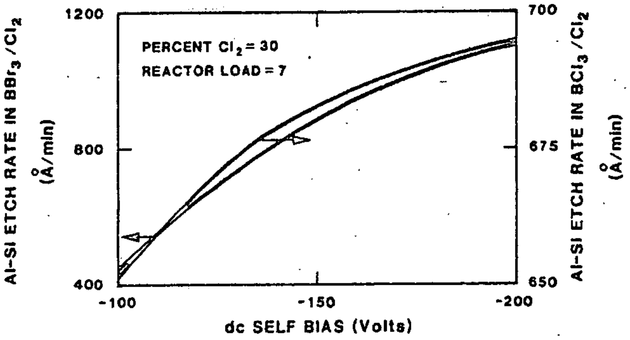

Fig. 4. Al-Si etch rate as a function of dc self-bias voltage in BX_3/Cl_2

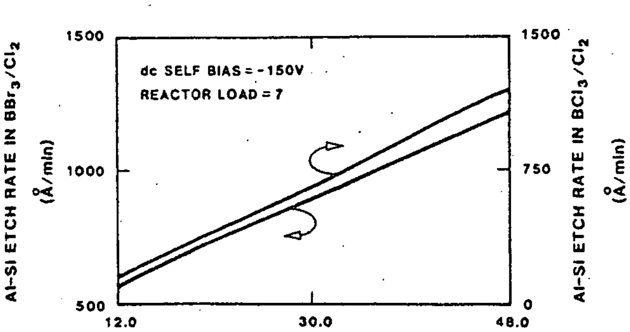

Fig. 5. Al-Si etch rate as a function of percent Cl_2 in BX_3/Cl_2

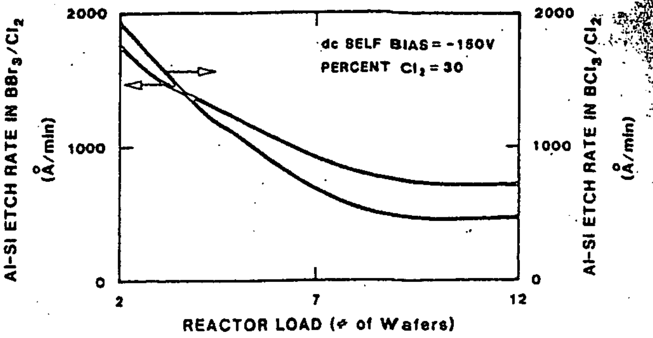

Fig. 6. Al-Si etch rate as a function of reactor load in BX_3/Cl_2

Selectivity and anisotropy.—The selectivity of etching Al over Si, SiO_2, and photoresist in both BBr_3/Cl_2 and BCl_3/Cl_2 decreases with increasing dc self-bias and increases with increasing Cl_2 fraction in the mixture. However, the selectivity of BBr_3/Cl_2 etching is significantly greater (as much as one order of magnitude) than BCl_3/Cl_2 under most conditions, as shown in Fig. 7 and 8. Not surprisingly, the ability of the two gas mixtures to etch features anisotropically, or with zero linewidth loss, are reversed with respect to the above noted variations in dc self-bias and percent chlorine in the mixture. This suggests that energetic ion bombardment is important to both gas mixtures for removing etch inhibitors and promoting directional etching. Figures 9 and 10 illustrate that BCl_3/Cl_2 has a larger window for anisotropic etching compared to BBr_3/Cl_2, but in both mixtures directionality in the etch is achieved only at low percent Cl_2 and high bias.

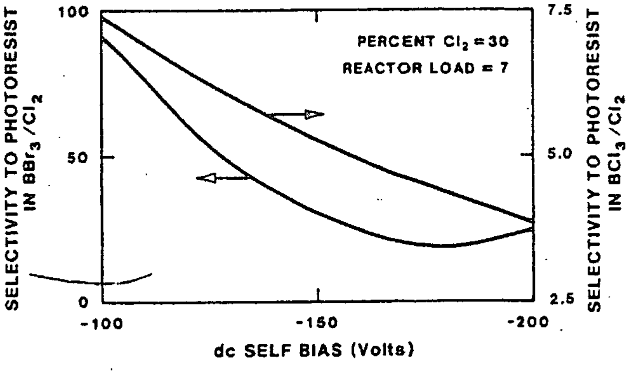

Fig. 7. Selectivity to photoresist as a function of dc self-bias in BX_3/Cl_2.

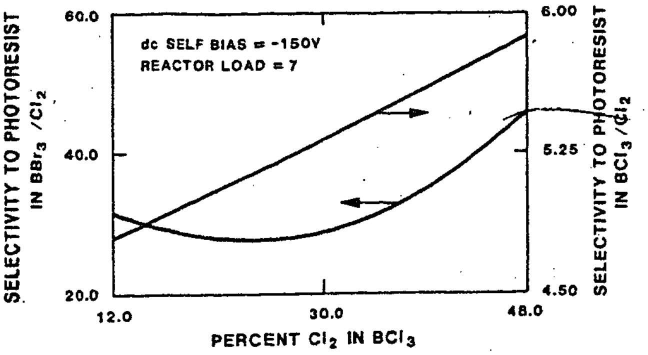

Fig. 8. Selectivity to photoresist as a function of percent Cl_2 in BX_3/Cl_2.

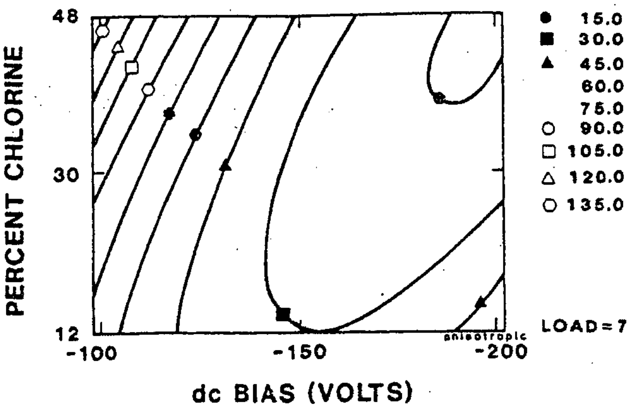

Fig. 11. Al/photoresist selectivity as a function of dc self-bias and percent Cl_2 in BBr_3/Cl_2.

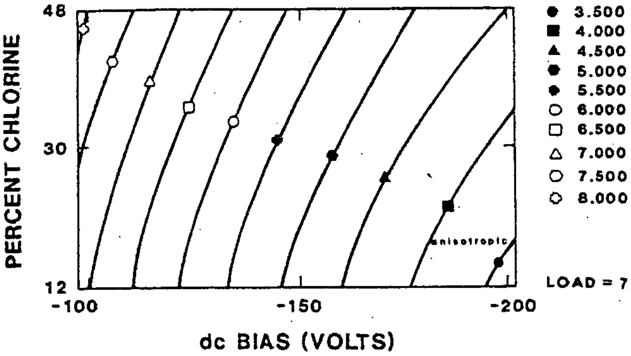

Fig. 12. Al/photoresist selectivity as a function of dc self-bias and percent Cl_2 in BCl_3/Cl_2.

Figures 11 and 12 show the achievable trade-offs between selectivity and anisotropy for the two gas mixtures. Use of BBr_3/Cl_2 has the penalty of a smaller window for anisotropic etching, but the achievable selectivity while maintaining anisotropic profiles is as much as an order of magnitude better than BCl_3/Cl_2. It is possible to achieve anisotropic profiles in Al films with BBr_3/Cl_2 mixtures while maintaining high Al/SiO_2 and Al/photoresist etch rate ratios. For example, anisotropic profiles are obtained at 10 mtorr total pressure, −200V dc self-bias, 30% chlorine in BBr_3, and a 12-wafer load, with an Al/SiO_2 etch rate ratio of 33:1 and an Al/photoresist etch rate ratio of 15:1, as shown in Fig. 13. Al/SiO_2 and Al/photoresist ratios of 13.5 and 2.5, respectively, are measured under similar conditions in BCl_3/Cl_2 mixtures. One final, interesting observation concerning anisotropy in BBr_3/Cl_2 plasmas was that anisotropy could be achieved easier with higher photoresist loading, implicating the importance of a sidewall polymer mechanism in promoting anisotropy. It should be noted that all samples in this work were etched to end point. Results from both etchant mixture types exhibit residue in the etched areas, and additional work on overetching requirements is warranted.

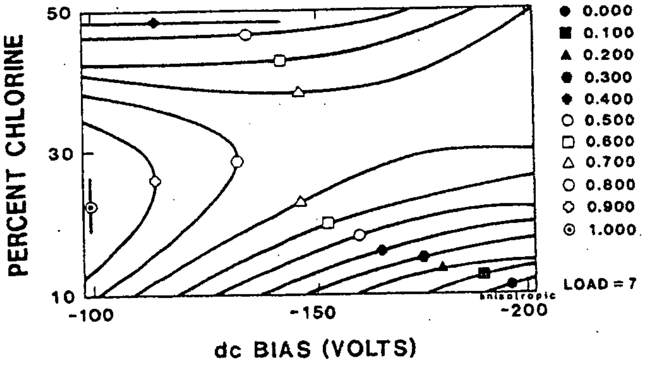

Fig. 9. Mean linewidth loss in microns as a function of dc self-bias and percent Cl_2 in BBr_3/Cl_2.

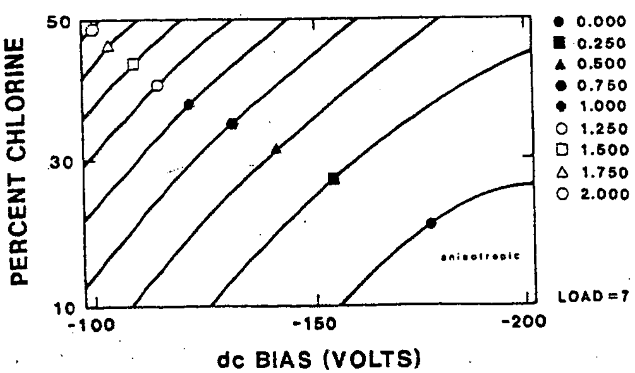

Fig. 10. Mean linewidth loss in microns as a function of dc self-bias and percent Cl_2 in BCl_3/Cl_2.

Discharge products and OES.—Interpreting the chemical identity of species present in a plasma from mass spectroscopic measurements made downstream of the discharge is fraught with difficulty due to the reactivity and marginal vapor pressures of the products and the transit times involved. Only a detailed simulation of the transit downstream could relate peak heights quantitatively to species abundance in the discharge [*e.g.*, Ref. (12, 13)], a task beyond the scope of this paper. Nevertheless, by comparing the mass spectra of products from BBr_3/Cl_2 discharges with those of BCl_3/Cl_2 under the same conditions, some qualitative indication may be gained about important distinctions in the plasma chemistry of the two mixtures which bring about differences in etch rates, selectivity, and anisotropy. The mass spectra traces of discharge products presented in Fig. 14-17 are uncorrected for analyzer sensitivity, variations in travel times of heavier species, etc. In analyzing this data, approximate correction factors have been considered in evaluating the traces.

The gain in the mass spectra peaks of Br and Cl shown in Fig. 14 and 15 indicates that greater dissociation of either parent BX_3 (X = Cl or Br) molecule occurs when the plasma is switched on, presumably as the result of electron collision reactions such as

$$BX_3(g) + e \rightarrow BX_2(g) + X(g) + e \qquad [2]$$

$$BX_3(g) + e \rightarrow BX(g) + 2X(g) + e \qquad [3]$$

Emission lines for Br at 448, 452, and 751 nm, and for Br^+ at 478 were also resolvable in the OES of BBr_3/Cl_2 discharges. Bromine emission appeared to increase with increasing dc self-bias, possibly indicating greater dissociation of BBr_3 at higher RF power. This is consistent with the consideration of free halide as an etchant species and higher etch rates observed at the higher dc self-bias.

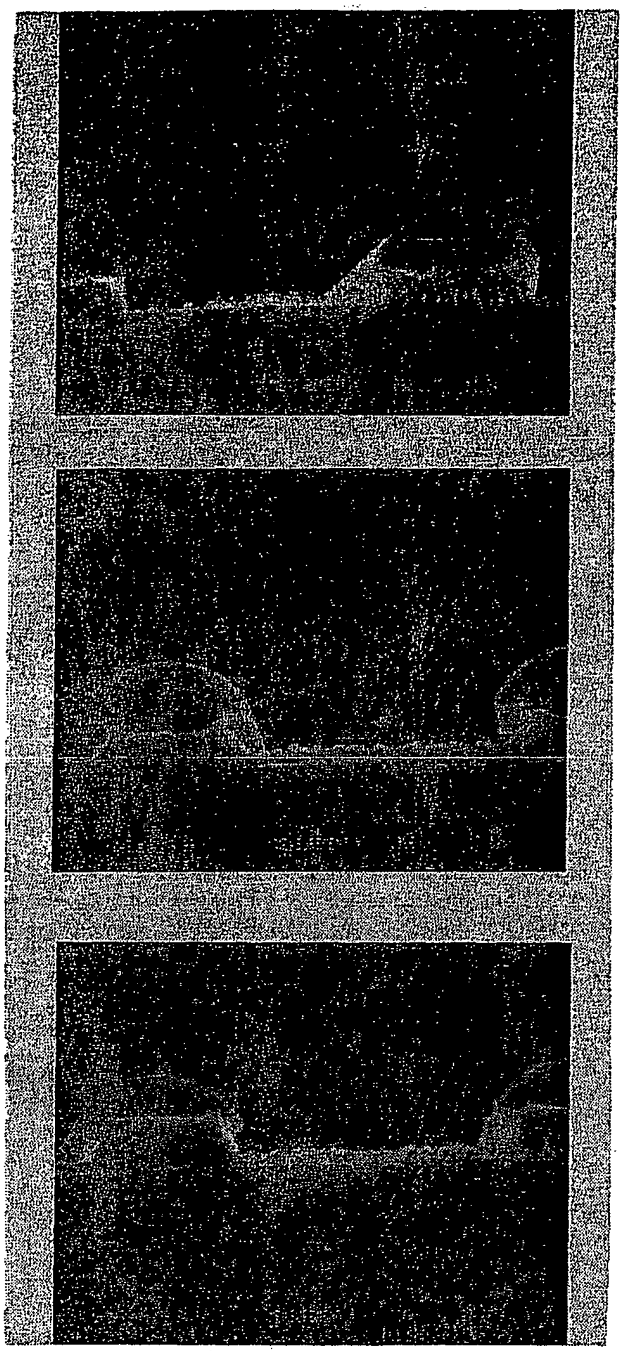

Fig. 13. Scanning electron micrographs of Al films etched in BBr_3/Cl_2: (a,top) etched at −200V dc self-bias, 30% Cl_2, 12 wafers; (b, center) etched at −100V dc self-bias, 30% Cl_2, 12 wafers; (c, bottom) etched at −200V dc self-bias, 30% Cl_2, 2 wafers.

Peaks due to HX^+ are also notable in the spectra as a result of traces of residual moisture contamination in the system and the pronounced affinity of boron trihalides for the oxygen in water (14). Oxygen scavenging occurs in the presence of either BBr_3 or BCl_3 through reactions such as

$$2BX_3 + 3H_2O \rightarrow B_2O_3 + 6HX \qquad [4]$$

$$2BX_3 + O_2 \rightarrow B_2O_3 + 3X_2 \qquad [5]$$

These scavenging reactions have been reported (15) to be about as favorable for BCl_3 as for BBr_3. Conversion of $B_2O_3(s)$ back to a volatile product can also occur through reaction with BX_3 to form trihaloboroxines, $(BOX)_3$

$$BX_3 + B_2O_3 \rightarrow (BOX)_3 \qquad [6]$$

Porter and Gupta (16) have noted the volatility of B_2O_3 is enhanced in the presence of boron halides. Figures 15 and 16 indicate that reaction [6] may be more favorable for BCl_3 since the relative concentration of BOBr is substantially less than the corresponding BOCl monomer.

Although oxygen scavenging reactions obviously consume some fraction of the BX_3 feed gas, quantitative consumption of BX_3 could not occur without slowing or stopping native oxide etching altogether. Since both BBr_3/Cl_2 and BCl_3/Cl_2 etch Al-oxide at a high rate, reactions [4]-[6] represent a minor loss mechanism for the boron trihalide and it is reasonable to expect a significant fraction of unreacted boron trihalide in the effluent. Shown in Fig. 15 and 17 is the fingerprint pattern of BCl^+, BCl_2^+, and BCl_3^+ detected in the products of BCl_3/Cl_2 discharges. This pattern is consistent with the reported cracking patterns of BCl_3 (10) and it indicates that substantial amounts of BCl_3 are present in the discharge products. However, for BBr_3/Cl_2 plasmas illustrated in Fig. 14 and 16, the analogous BBr^+ and BBr_2^+ fingerprint reported by Koski *et al.* (10) is conspicuously absent (or at least three orders of magnitude less than the cracking fragments of BCl_3). This suggests that either the parent molecule, BBr_3, is more completely dissociated in the discharge or that the BBr_3 is tied up in higher molecular weight species which never reach the mass spectrometer. This observation cannot be explained by simple consumption in etching due to the large magnitude of species involved.

There are indications in the distribution of discharge products that the latter interpretation is more consistent. For BBr_3/Cl_2 plasmas in a feed gas molar ratio of seven to three, the relative concentrations of atomic Br and molecular HBr shown in Fig. 14 are small compared to the concentrations of Cl and HCl, even after correcting the mass spectrometer signal for transit time, background, and analyzer sensitivity error. If electron impact dissociation of the boron trihalide feed gas was more quantitative in BBr_3, as has been suggested (6) based on the relatively weak B-Br bond strength, the relative strength of the bromine signal should be substantially stronger, more in line with the molar ratio of BBr_3 in the feed gas. Furthermore, the B^+ signal in the mass spectra might be expected to increase due to ionizer cracking of radical BBr_x species in the discharge products. However, Fig. 14 and 15 show that a relatively large B^+ peak is detectable in BCl_3/Cl_2 discharge products, whereas it is completely absent in the BBr_3/Cl_2 spectra.

Although the distribution of discharge products do not quantitatively establish the extent of electron impact induced dissociation of BBr_3, the distribution suggests that the products of dissociation are removed more efficiently through rapid gas-phase recombination reactions, compared to BCl_3. The exact nature of the product of such recombination reactions is not known at this time. However, it is important to note that BBr_3/Cl_2 discharges had a greater tendency to leave powdery residues behind on the reactor chamber walls, compared to BCl_3/Cl_2 discharges. The powdery residue had a yellow-green or brownish color to it, suggestive of uncharacterized, mixed, boron subhalides (17). By comparison, BCl_3/Cl_2 discharges tended to leave a white, powdery residue (further elemental analysis of these residues are in progress).

Auger spectroscopy.—Keaton and Hess (6) have suggested that differences in the ability of BBr_3 and BCl_3 to etch native aluminum oxide may be related to the formation of B_2O_3 residues which could inhibit aluminum oxide etching. If B_2O_3 formation were a more significant problem in BBr_3/Cl_2 discharges, compared to BCl_3/Cl_2, it stands to reason that a greater level of substrate contamination should be detectable in postetched wafers, since B_2O_3 is a stable solid product. A B_2O_3 residue hypothesis is inconsistent with Auger surface analysis performed in this study which shows BBr_3/Cl_2 is no worse and is perhaps better than BCl_3/Cl_2 with regard to substrate contamination. Test die from samples etched with each gas mixture were examined for detectable levels of boron, oxygen, bromine, and chlorine by SAM point-mode survey spectra. Pad areas of the aluminum still covered by photoresist and exposed areas of SiO_2 were surveyed in an as received condition and after 2 kV Ar ion sputter clean. The as received

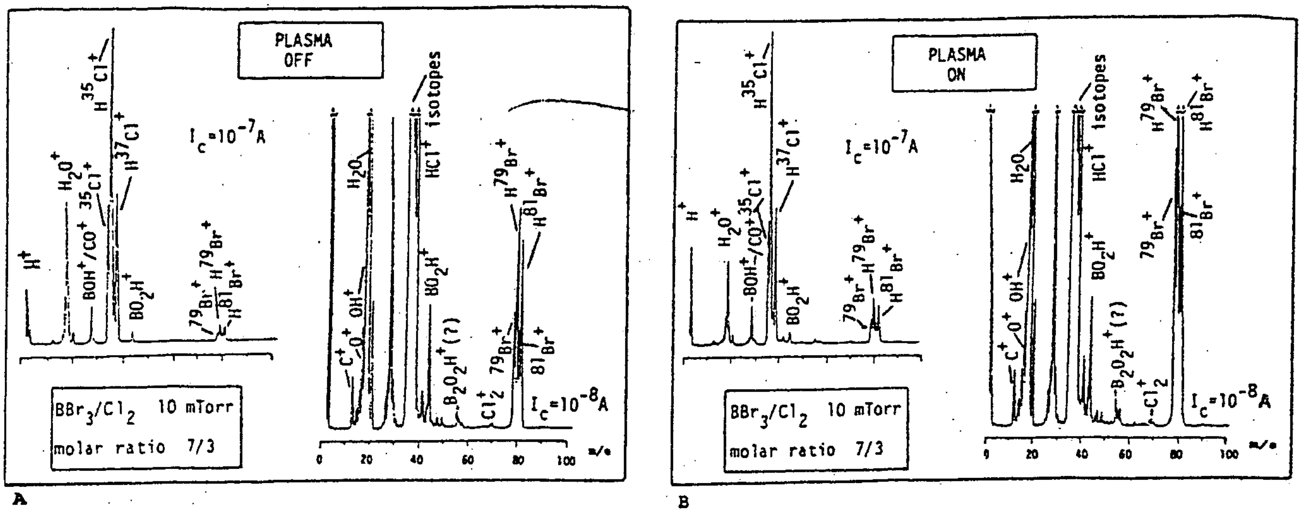

Fig. 14. Mass spectra of BBr_3/Cl_2 discharge products in the 1-100 amu range: (A) plasma off; (B) plasma on

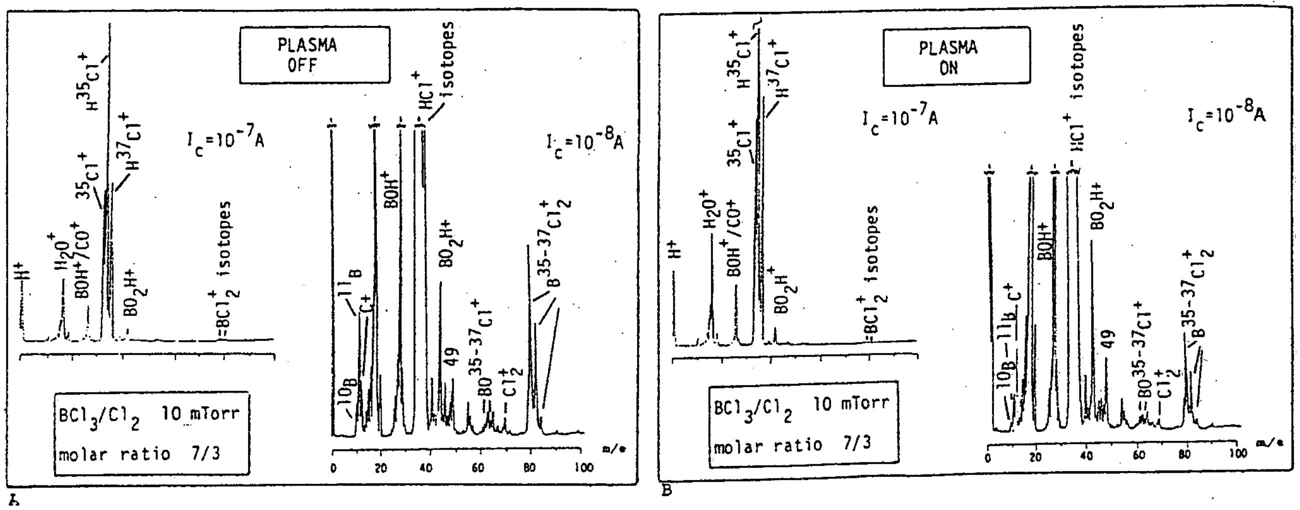

Fig. 15. Mass spectra of BCl_3/Cl_2 discharge products in the 1-100 amu range: (A) plasma off; (B) plasma on

samples etched in BBr_3/Cl_2 revealed only small amounts of Al and O contaminants on these surfaces, as opposed to the BCl_3/Cl_2 samples which showed 0.7 and 4 atomic percent (a/o) Cl, and 1.5 and 0.2 a/o Al found on the photoresist pad and SiO_2, respectively. Examination of the Al/photoresist interface after sputter beam clean did not reveal any contaminants other than a trace amount of oxygen from the native oxide for either sample. No boron or bromine could be detected on the BBr_3/Cl_2 etched sample.

Kinetic model of BBr_3/Cl_2 etching.—The key to understanding the kinetics of BBr_3/Cl_2 plasma etching of Al and the significant improvements in selectivity achieved with these mixtures appears to lie in the chemical mechanism responsible for (*i*) the lack of BBr_3 or BBr_x products downstream from the discharge, (*ii*) a significant yellow-brown residue formation in the reactor chamber, and (*iii*) the previously noted (6) surface temperature dependence of Al-oxide plasma etching in BBr_3. Each of these observations implies that recombination reactions involving BX_x radicals, either in the gas phase or at the wall, are considerably more important in BBr_3/Cl_2 plasmas, as opposed to BCl_3/Cl_2 plasmas. Yet, despite the apparent importance of recombination, BBr_3 exhibits distinct differences from etchant gases such as CCl_4, well-known for excessive recombinant behavior leading to thick polymeric deposits. The recombinant behavior of BBr_3 appears to be intermediate between CCl_4 and BCl_3, sharing aspects of both.

To illustrate this fact, it is necessary to compare previously reported findings regarding BBr_3, BCl_3, and CCl_4 discharges, and contrast those findings to the BBr_3/Cl_2 results. The surface temperature dependence of Al-oxide etching in BBr_3 plasmas has been shown by Keaton and Hess (6) to be almost identical to that measured by Tokunaga and Hess (18) for CCl_4 plasmas. In both cases, this surface temperature dependence has been used to strongly suggest residue inhibition of etching, presumably formed through recombination either in the gas phase or at the wall. Conversely, aluminum etching in either BBr_3 or BCl_3 has been shown to have no surface temperature dependence, whereas CCl_4 does, apparently due to the continued influence of residue inhibition. This surface temperature dependence of BBr_3 etch rates indicates that the chemical behavior is similar in ways to both BCl_3 and CCl_4. However, the chemical mechanism responsible for this similarity is not clear. In the case of CCl_4 plasmas, the formation of dimers, C_2Cl_4, in abundance, has been strongly implicated as the precursor leading to film deposits that inhibit etching. Since boron halides do not form polymers in the same fashion as chlorocarbons, attention has been focused away from analogous precursors in boron halide chemistry having a similar role in the formation of etch inhibitors. For example, Keaton and Hess (6) suggest instead that B_2O_3 residues are responsible in boron halide chemistry for etch inhibition. However, this hypothesis is inconsistent with the surface analysis performed on samples etched in BBr_3/Cl_2 and the preliminary indications about the chemical nature of residues left in the reactor chamber.

The above data suggest that alternative mechanisms for the formation of etch inhibiting compounds may be important in controlling the etch characteristics of BBr_3/Cl_2 etching. For example, it is largely unrecognized that dis-

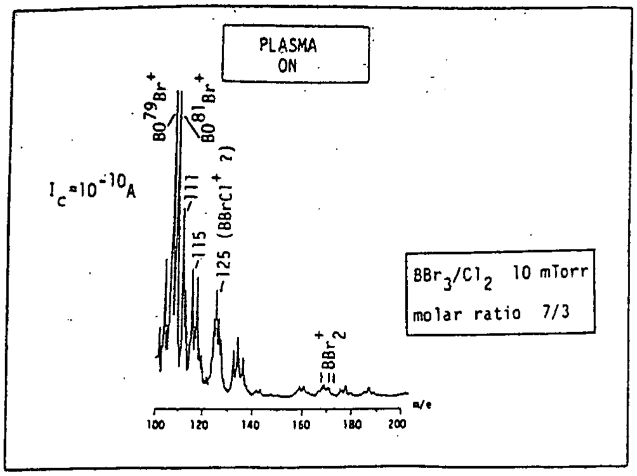

Fig. 16. Mass spectra of BBr_3/Cl_2 discharge products in the 100-200 amu range.

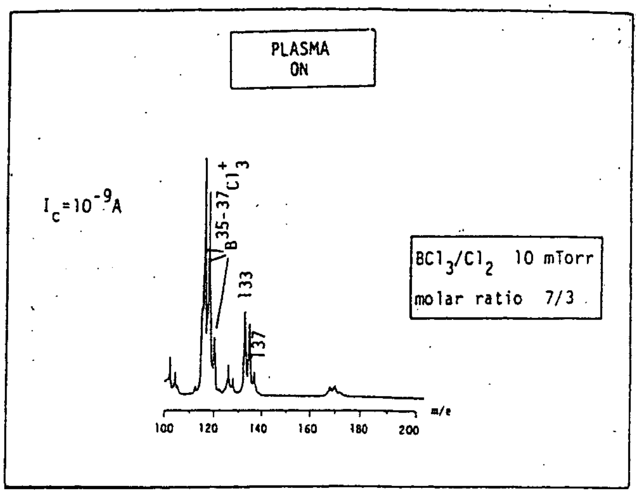

Fig. 17. Mass spectra of BCl_3/Cl_2 discharge products in the 100-200 amu range.

charges have been used as a preparation technique for the synthesis of diboron tetrahalides, B_2Br_4, and that the technique is strikingly similar to the conditions actually employed for plasma etching metal films. It is known that when BBr_3 is passed at low pressure through a RF glow discharge, B_2Br_4 is formed, and that on further exposure to the discharge, B_2Br_4 very rapidly disproportionates to B_nBr_n (n = 7-10) (19-21). Controversy exists as to whether it is the BBr or BBr_2 radical (both of which easily form in the discharge) which attacks the parent BBr_3 molecule and leads to the dimerization reaction (21). However, the reaction sequence in the discharge is thought to be

$$BBr_3 + e \rightarrow BBr + 2Br + e \quad [7]$$

$$BBr + BBr_3 \rightarrow B_2Br_4 \quad [8]$$

Although $\Delta G_f(B_2Br_4)$ is unknown, Briggs *et al.* (21) note the value is likely to be highly negative. Presumably, further insertion of BBr fragments leads to the formation of intermediate open cages of boron atoms which, dependent on reactor conditions, change to stable closed cage derivatives (19)

$$nBBr + B_2Br_4 \rightarrow B_nBr_n + 2Br \quad [9]$$

Mixed subhalides, $B_nBr_{n-m}Cl_m$ (n is most often equal to 9, m is equal to 1-4), are also known to readily form in the presence of Cl_2 through substitution reactions, and have been reported to leave yellow-orange and brown thin film deposits (17, 19, 21).

Dimer and subhalide formation reactions are not unique to BBr_3 plasmas; BCl_3 is known to form B_2Cl_4 in an analogous fashion (19-24). However, there is evidence that the bromide dimers are more stable than the corresponding chloride and this could readily explain variations in the etch behavior between the two gas mixtures. The dimer, B_2Cl_4, is known to be liable to attack from more electronegative species, *i.e.*, Cl_2 (25)

$$B_2Cl_4 + Cl_2 \rightarrow 2BCl_3 \quad [10]$$

and it is known to undergo replacement reactions with BBr_3 (23, 24)

$$3B_2Cl_4 + 4BBr_3 \rightarrow 3B_2Br_4 + 4BCl_3 \quad [11]$$

The B—B bond length of the dimers has been observed to be shorter (and hence stronger) in B_2Br_4 compared to the corresponding chlorine dimer (26, 27). Finally, it has been observed that boron halide dimer deposits are unstable to oxygen at room temperature (24) and the reaction is quite violent. The explosiveness of this reaction suggests that few residual dimeric deposits would remain on the wafer after removal from the hexode reactor, and that little detectable residue would be left on samples used in Auger analysis.

Preparation procedures for B_2Br_4 usually call for the presence of a metal surface (notably Cu or Hg) in addition to the discharge, and it is thought that the metal acts as a trap, minimizing free halide cleavage of boron-boron bonds. Therefore, the presence of metal reactor walls (the chamber walls, *i.e.*, grounded electrode, of the hexode reactor used in BBr_3/Cl_2 RIE are made of stainless steel) and/or substrates in plasma etch reactors may exert a significant influence on the extent of these reactions. Surface effects in the plasma environment have been shown previously (18) to have a significant impact on dimerization rates in CCl_4 plasmas, with the conversion of CCl_4 to C_2Cl_4 reaching 8.3 weight percent (w/o) with stainless steel electrodes. Kutz and Morrison (20) have reported an approximately 2.0 w/o conversion of BBr_3 to B_2Br_4 in a discharge in the presence of mercury. Under these circumstances, it is apparent that dimerization reaction rates for BBr_3 can approach those of CCl_4, an indication of their potential importance.

The chemical mechanism responsible for the improvements in selectivity achievable with BBr_3/Cl_2 plasmas is not clear in its entirety at this time. However, there is significant circumstantial evidence to indicate that diboron tetrabromides and boron subbromides formed from reactions [7]-[9] play a crucial role. If boron dimers and boron subbromide species (perhaps even with the assistance of photoresist products) formed films which adsorbed to the surface, they would have to undergo dissociation to provide BBr_x species capable of reacting with the native oxide. Dissociation on the surface could be accomplished either through raising the surface temperature or by increasing ion bombardment by increasing dc self-bias, illustrating the synergism of both physical and chemical mechanisms in Al native oxide etching. Alternatively, the greater reactivity of the Al surface may be effective in bringing about a spontaneous, dissociative chemisorption of linked, BBr_x species, thus shutting off the chain or cage building process. These types of distinctions could lead to an explanation for the variation in surface temperature reactivity dependence from either CCl_4 or BCl_3. Under any circumstances, the proposed greater role for recombination reactions in BBr_3/Cl_2 plasmas which may lead to a higher molecular weight compounds is consistent with the observed smaller window in the parameter space for anisotropic etching (less ions available to assist in etching), etchant depletion effects with reactor loading, mass spectra data, and the increased selectivity of the etching with BBr_3 (greater chemistry influence).

Physically, the improvements in selectivity observed with BBr_3/Cl_2 over BCl_3/Cl_2 can be understood best in the context of an ion flux model, somewhat akin to Zarowin's (28) ion energy transport model. Selectivity and anisotropy control in BCl_3/Cl_2 discharges conform well to Zarowin's concept that the ratio of neutral to ionic etch chemistry determines these features. RIE in BCl_3/Cl_2 discharges appears to have a large physical, sputter-erosion process component. Hence, low selectivity toward etching aluminum over photoresist, Si, or SiO_2 is observed. RIE in BBr_3/Cl_2 is a more complex combination of physical and chemical processes. The improvement obtained in BBr_3/Cl_2 is probably related to a reduction in ion etch component of the plasma chemistry. Dimers and higher order subbromides formed in the discharge may play a large role in regulating the neutral and ionic etch component through removing the parent BBr_3 (from which ions form in electron collision reactions) or through adsorbing to surfaces. Although the evidence presented in this study is indirect, dimerization and subhalide formation does occur in discharges and may represent an important aspect of plasma etching of Al films. Further study of this chemistry is needed.

Conclusions

Selective and anisotropic reactive ion etching of Al in a hexagonal cathode reactor can be achieved with either BBr_3/Cl_2 or BCl_3/Cl_2 mixtures. Parallel trends in Al etch rates and selectivities are observed for the two gas mixtures though performance is quantitatively different. The major differences as gleaned from the mass spectra apparently stem from the absence of BX_x fragments in the BBr_3/Cl_2 mixtures. This may underscore the need to consider the importance of dimerization and boron subhalide formation reactions which are known to occur in boron halide discharges. Including such reaction pathways in a kinetic model for Al etching provides a means of consistently resolving variations in the etch behavior of two seemingly similar etchant gas mixtures. Under proper conditions, the BBr_3/Cl_2 process is capable of as much as an order of magnitude improvement in selectivity over SiO_2 and photoresist compared to the BCl_3/Cl_2 process, while maintaining anisotropic profiles.

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